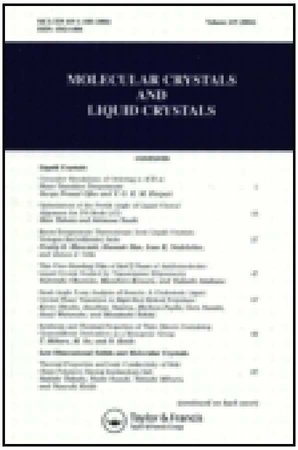

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Single Crystal Preparation of DAST for Terahertz-Wave Generation

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Single Crystal Preparation of DAST for Terahertz-Wave Generation

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DAST (1-methyl-4-{2-[4-(dimethylamino)phenyl]ethenyl}pyridinium p-toluenesulfonate) is a promising crystalline material for electro-optic applications and THz-wave generation. DAST powder for crystal growth was prepared by two synthesis routes including the conventional one and we confirmed that purity of DAST powder became indistinguishable after proper recrystallization even using conventional synthesis process. The highest solubility of DAST was found for methanol-acetonitrile mixture, and DAST crystal growth in this mixture or methanol-ethanol mixture gave thicker crystals than those grown in methanol. Thus, morphological control of DAST single crystals was found to be possible by varying solvents.

Keywords: crystal growth; DAST; ionic dye; organic crystal; second-order nonlinear optics; THz-wave generation

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INTRODUCTION

Organic ionic crystal DAST (1-methyl-4-{2-[4-(dimethylamino)phenyl]ethenyl}pyridinium *p*-toluenesulfonate) has attracted attention for its large second-order nonlinear optical properties [1], and its single crystal growth and application for electro-optic devices have been extensively investigated [2]. After Zhang *et al*. reported pulsed THz-wave generation with a broad range spectrum from DAST using optical rectification [3], DAST was noticed as a crystalline material for THz-wave generation as well. Different frequency generation was also applied for DAST to generate tunable THz-waves [4]. The tunable range is from 2 THz to 30 THz [5], which is quite wide compared with semiconductors such as gallium phosphide, lithium niobate etc. Although DAST is a promising THz-wave generation material, improvement of crystal quality has been an important issue to be solved.

In this connection, we reexamine the synthesis route of DAST and recrystallization process was optimized since purity of DAST powder crystals used for crystal growth seemed to influence on the quality of the grown crystals. For DAST crystal growth, methanol has been generally used because of the highest solubility among the conventional organic solvents [6]. Accordingly, solution crystal growth with slow cooling process in methanol has been mainly utilized to prepare quality crystals of DAST, and morphological control of crystals was not so easy due to limited valuable factors. Thus, DAST crystal growth using methanol, ethanol, acetonitrile, and their mixed solvents was also investigated.

EXPERIMENTAL

DAST was prepared by the following two routes shown in Figure 1. Route A is the conventional process to prepare DAST derivatives [7]. At first, γ-picoline **1** was reacted with methyl *p*-toluenesulfonate **2**, and the resulting pyridinium salt **3** was condensed with benzaldehyde **4** to give DAST. In the second route (Route B), 4-bromo-*N,N*-dimethylaniline **5** was coupled with 4-vinylpyridine **6** using a palladium catalyst [8], and the obtained stilbazol **7** was methylated by using methyl *p*-toluenesulfonate **2** to give DAST.

Solubility of DAST was evaluated as follows. At first, enough amount of DAST was put in a solvent and heated at a certain temperature. After keeping at the temperature for 6 h and confirming that DAST powder has still remained, 10 ml of the saturated supernatant solution was taken out and the solvent was evaporated under a

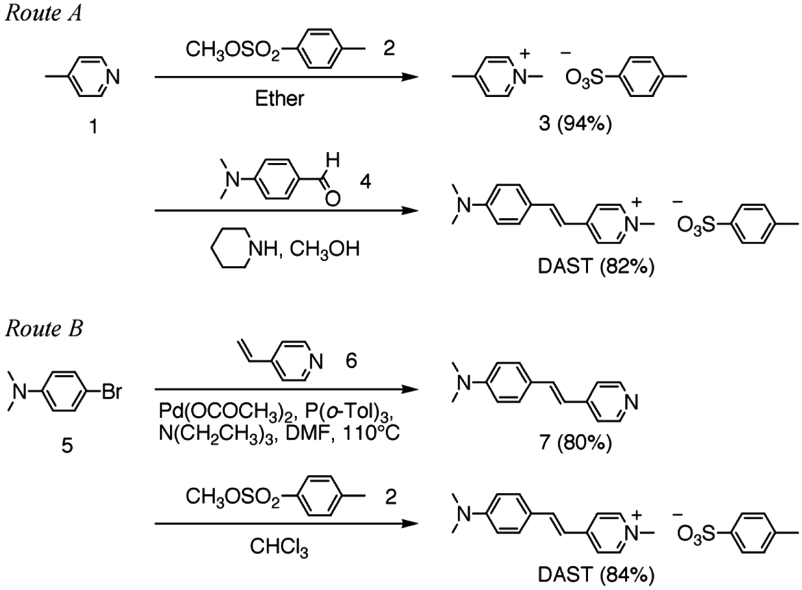

FIGURE 1 Two synthesis procedures of DAST.

reduced pressure. By weighing the DAST crystals remained, solubility at the temperature was calculated.

DAST single crystals were grown from its solution by the slow cooling method. General procedure was as follows: In a 500 ml PFA wide-mouth bottle (Flonchemical NR-191), a certain amount of DAST and 200 ml of solvent were added. The input amount of DAST was set to soluble amount in the saturated solution at 45°C. In the solution, a teflon board with straight grooves was sunk to perform the slope nucleation method [9]. The bottle was tightly sealed by a stopper and a screw cap and it was put in a programmable temperature-controlled water bath. The temperature was first kept at 55°C for 10 h and DAST was completely dissolved with stirring. After that, the temperature was cooled to 45°C for 4 h. Then, the temperature was lowered with cooling rate of 0.1°C/day in general.

RESULTS AND DISCUSSION

DAST was prepared by the two routes for comparison. In the second step of Route A, a basic catalyst such as piperidine is added for the condensation reaction and water is naturally produced as a byproduct. On the other hand, in the second step of Route B, catalyst is not necessary and only the desired product is obtained, indicating that purer DAST is obtained just after the final reaction. This synthesis route was used to prepare DAST thin films by the chemical vapor deposition [10]. At first, non-solvent reaction was performed in the second step of Route B. However, the yield of the step was low (34%). When chloroform was used as solvent in this step, the yield increased up to 84%. The total yield from the starting compound in Route A was 77%, which is slightly higher than that of Route B (67%). As was expected, the DAST crystal purity just after the final reaction of Route B was higher than those of Route A, which was evaluated by elemental analysis. However, after recrystallizing from methanol and then from ethanol, the purity of DAST crystals obtained from both routes became the same. Thus, we confirmed that conventional Route A can be used to prepare pure DAST when its proper recrystallization is performed.

Figure 2 shows the solubility curves of DAST for methanol, ethanol, acetonitrile and their mixed solvents at around 45°C. The order of the solubility in pure solvents is methanol $>>$ ethanol $>$ acetonitrile. Since dielectric constants (ε) of methanol, ethanol and acetonitrile at 25°C are 32.7, 24.6 and 35.9, respectively, solubility of DAST in these solvents cannot be explained only by ε. Hydroxyl protons of alcohol seem to be important for solvation. However, methyl group of methanol is also important to increase solubility of DAST since DAST solubility in water is less than that of methanol. When methanol and ethanol was mixed in 1:1 volume ratio, the solubility became intermediate between that of methanol and ethanol, indicating that solvation ability was averaged. On the other hand, when acetonitrile was mixed with methanol or ethanol in 1:1 volume ratio, solubility of DAST increased about twice or more of that in pure alcohols. Especially, methanol-acetonitrile binary system shows the highest solubility of DAST among the solvent investigated so far. Figure 3 displays variation of the solubility at 45°C depending on the content of methanol in the methanol-acetoritrile mixed solvent. Solubility of DAST in the 3:1 mixture was quite augmented up to 64.5 $\mathrm{gL^{-1}}$, which was already near to the maximum solubility of 68.0 $\mathrm{gL^{-1}}$ observed in 1:1 mixture. Further increase of acetonitrile content in the mixed solvent decreased DAST solubility. Increase of DAST solubility in methanolic solution by adding other solvent with larger ε than methanol was also observed in methanol-water mixture [11].

Referring to the solubility curves of DAST, we performed its crystal growth in these solutions by slow cooling from 45°C. From methanol solution, we obtained DAST single crystals with a plate-like shape, in which crystallographic a-axis (the polar axis) and b-axis are on the developed plane and c-axis is nearly along the thickness direction

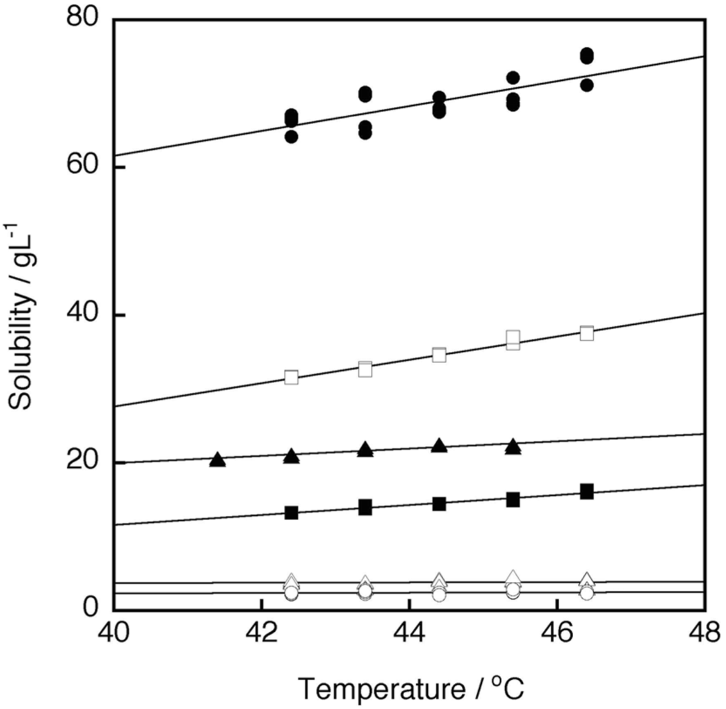

FIGURE 2 Solubility curves of DAST in pure methanol, ethanol, acetonitrile and their mixed solvents: □ methanol; △ ethanol; ○ acetonitrile; ■ methanol-ethanol (1:1); ▲ ethanol-acetonitrile (1:1); ● methanol-acetonitrile (1:1).

[12]. However, pure ethanol and acetonitrile solutions and ethanol-acetonitrile mixed solution only gave tiny crystals less than 1 mm in side. From methanol-acetonitrile mixed solution, we obtained thicker crystals. This morphological change is important for applications. In order to generate THz-waves, the laser was input perpendicular to the developed *ab*-plane so far. In this case, the pass length of the incident beam is limited by the thickness of the crystal. However, thick DAST crystals may be able to generate THz-waves by passing through the laser beam along *b*-axis, i.e., parallel to the *ab*-plane. In this case, we can use more interaction length of the crystal. From methanol-ethanol mixture, thick crystals were also obtained. Rai *et al*. reported DAST crystal growth in methanol-ethanol mixture and similar tendency was described [13]. Although the dimension of the developed face became smaller compared with the case of methanol solution, it seems to be improved by controlling nucleation and crystal growth rate.

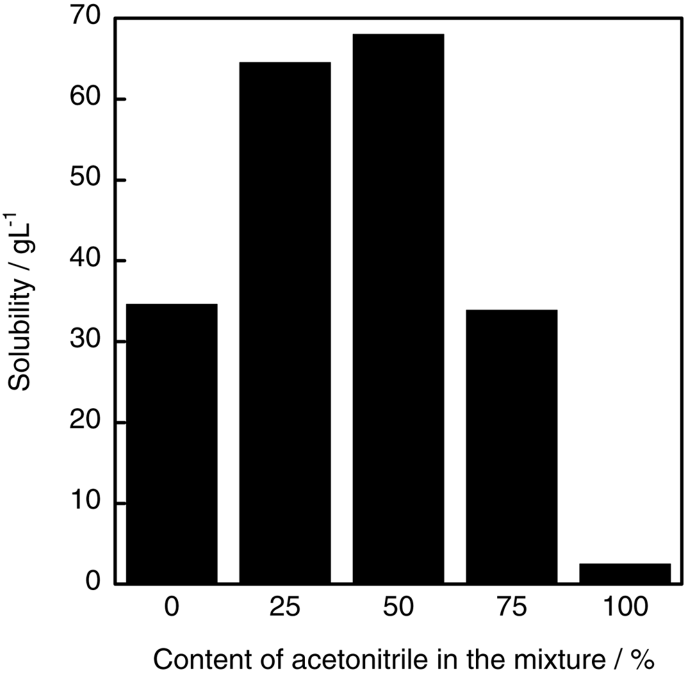

FIGURE 3 Solubility of DAST in methanol-acetonitrile binary system at 45°C.

Terahertz-wave generation properties of the crystals were not deteriorated by changing the solvent from methanol to methanol-ethanol mixture when appropriate crystal growth conditions were selected.

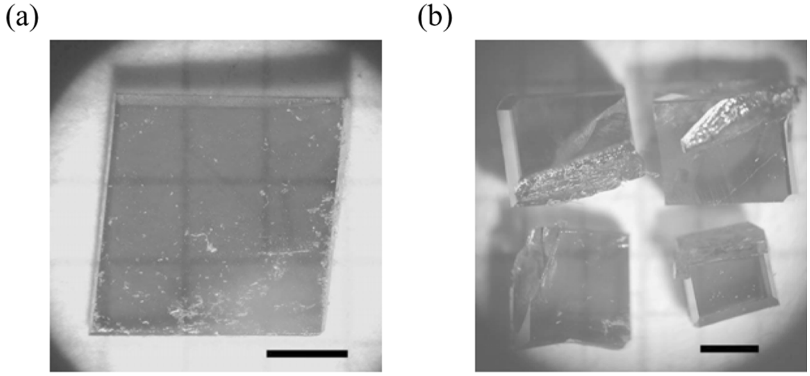

FIGURE 4 DAST crystals obtained from (a) methanol solution and (b) methanol-acetonitrile (1:1) solution. Bars indicate 1-mm length.

In conclusion, we confirmed that DAST crystalline powder as a starting material for crystal growth can be purified by recrystallization from methanol and ethanol irrespective of synthesis routes. Highest solubility of DAST among organic solvents was found in methanol-acetonitrile mixture. By using this mixture or methanol-ethanol mixture as solvents for DAST crystal growth, we obtained its crystals thicker than those from methanol. These findings show possibility of single-crystal morphological control of DAST and its derivatives [14] and the resulting expansion of their device applications is expected.

REFERENCES

[1] (a) Okada, S., Matsuda, H., Nakanishi, H., Kato, M., & Muramatsu, R. (1986). Japan Patent Application 61-192404.
  (b) Okada, S., Matsuda, H., Nakanishi, H., Kato, M., & Muramatsu, R. (1992). Japan Patent 1716929.
  (c) Nakanishi, H., Matsuda, H., Okada, S., & Kato, M. (1989). *Mater. Res. Soc. Int. Mtg. Adv. Mater.*, *1*, 97.
  (d) Marder, S. R., Perry, J. W., & Schaefer, W. P. (1989). *Science*, *245*, 626.

[2] (a) Pan, F., Knöpfle, G., Bosshard, C., Follonier, S., Spreiter, R., Wong, M. S., & Günter, P. (1996). *Appl. Phys. Lett.*, *69*, 13.
  (b) Sohma, S., Takahashi, H., Taniuchi, T., & Ito, H. (1999). *Chem. Phys.*, *245*, 359.
  (c) Thakur, M., Xu, J. J., Bhowmik, A., & Zhou, L. G. (1999). *Appl. Phys. Lett.*, *74*, 635.

[3] Zhang, X.-C., Ma, X. F., Jin, Y., Lu, T.-M., Boden, E. P., Phelps, P. D., Stewart, K. R., & Yakymyshyn, C. P. (1992). *Appl. Phys. Lett.*, *61*, 3080.

[4] (a) Kawase, K., Mizuno, M., Sohma, S., Takahashi, H., Taniuchi, T., Urata, Y., Wada, S., Tashiro, H., & Ito, H. (1999). *Opt. Lett.*, *24*, 1065.
  (b) Taniuchi, T., Okada, S., & Nakanishi, H. (2004). *J. Appl. Phys.*, *95*, 5984.

[5] Taniuchi, T., Adachi, H., Okada, S., Sasaki, T., & Nakanishi, H. (2004). *Electron. Lett.*, *40*, 549.

[6] Takayama, K., Yoshida, N., Deng, H.-H., Komatsu, K., & Kaino, T. (2000). *Nonlinear Opt.*, *25*, 413.

[7] Sakai, K., Yoshikawa, N., Ohmi, T., Koike, T., Umegaki, S., Okada, S., Masaki, A., Matsuda, H., & Nakanishi, H. (1990). *Proc. SPIE*, *1337*, 307.

[8] Hassner, A., Birnbaum, D., & Loew, L. M. (1984). *J. Org. Chem.*, *49*, 2546.

[9] Mori, Y., Takahashi, Y., Iwai, T., Toshimura, M., Yap, Y. K., & Sasaki, T. (2000). *Jpn. J. Appl. Phys.*, *39*, L1006.

[10] Burrows, P. E., Forrest, S. R., Sapochak, L. S., Schwartz, J., Fenter, P., Buma, T., Ban, V. S., & Forrest, J. L. (1995). *J. Cryst. Growth*, *156*, 91.

[11] Mineno, Y., Okada, S., Glavcheva, Z., Umezawa, H., Odani, T., Ikeda, S., Taniuchi, T., & Nakanishi, H. (2005). *Nonlinear Opt. Quant. Opt.*, *34*, 53.

[12] (a) Pan, F., Wong, M. S., Bosshard, C., & Günter, P. (1996). *Adv. Mater.*, *8*, 592.
  (b) Adachi, H., Takahashi, Y., Mori, Y., & Sasaki, T. (1999). *J. Cryst. Growth*, *198/199*, 568.

[13] Rai, R. N., Jeng, J. M., Tai, C. Y., & Lan, C. W. (2002). *J. Chin. Inst. Chem. Engrs.*, *33*, 461.

[14] Glavcheva, Z., Umezawa, H., Mineno, Y., Odani, T., Okada, S., Ikeda, S., Taniuchi, T., & Nakanishi, H. (2005). *Jpn. J. Appl. Phys.*, *44*, 5231.